Polymer Electrolyte Membrane Technology for Fuel Cells

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Abstract

The concept of using an ion-exchange membrane as an electrolyte separator for polymer electrolyte membrane (PEM) fuel cells was first reported by General Electric in 1955. However, a real breakthrough in PEM fuel cell technology occurred in the mid-1960s after DuPont introduced Nafion®, a perfluorosulfonic acid membrane. Due to their inherent chemical, thermal, and oxidative stability, perfluorosulfonic acid membranes displaced unstable polystyrene sulfonic acid membranes. Today, Nafion® and other related perfluorosulfonic acid membranes are considered to be the state of the art for PEM fuel cell technology. Although perfluorosulfonic acid membrane structures are preferred today, structural improvements are still needed to accommodate the increasing demands of fuel cell systems for specific applications. Higher performance, lower cost, greater durability, better water management, the ability to perform at higher temperatures, and flexibility in operating with a wide range of fuels are some of the challenges that need to be overcome before widespread commercial adoption of the technology can be realized. The present article will highlight the membrane properties relevant to PEM fuel cell systems, the development history of perfluorosulfonic acid membranes, and the current status of R&D activities in PEM technology.

Keywords: *ionic conductivity, Nafion®, perfluorosulfonic acid membranes, PEM fuel cells, polymer electrolyte membranes, proton-exchange membranes.*

Introduction

Among the various fuel cell systems known today, the proton-exchange membrane fuel cell system has proven to be an attractive and more promising option than alkaline, solid oxide, or molten carbonate fuel cell systems for power generation in portable, stationary, and mobile (automotive) applications. The use of proton-exchange membranes as an electrolyte separator in fuel cell applications offers several advantages, such as selectivity, system simplicity, and improved reliability compared with systems based on a liquid electrolyte. An early breakthrough in proton-exchange membrane technology occurred in 1955 when General Electric announced their successful demonstration of fuel cell operation with the first concept membrane, poly(styrene sulfonic acid). However, the system had a limited lifetime (<200 h) and failed prematurely due to membrane degradation by peroxide attack at the benzylic hydrogen. Further work on modifying the poly(styrene sulfonic acid) with cross-linking, partial fluorination, and blending with fluoropolymers improved the system lifetime to 1000 h, but still not into an acceptable range (>5000 h).[1–3]

A real breakthrough in the technology occurred in the mid-1960s when DuPont introduced a perfluorinated ionomer membrane under the trade name Nafion®.[4] The perfluorosulfonic acid (PFSA) membrane material provided superior mechanical and electrochemical properties and represented the first durable and stable polymer electrolyte membrane (PEM) fuel cell system. After extensive evaluation, Nafion® was first used by GE in 1966 for NASA's space mission work.[5,6] In extended operation, a multicell stack constructed with Nafion® membranes demonstrated more than 60,000 h of stable operation, thereby providing the exceptional lifetime needed for commercial fuel cells.[7] This advance resulted in worldwide acceptance of PEM fuel cells as a viable technology option. This article will highlight the membrane properties relevant to PEM fuel cell systems, the development of perfluorosulfonic acid membranes, and the current status of research and development activities involving PEM technology.

PEM Requirements

A schematic representation of the operating principles for PEM fuel cells is detailed in Figure 1. The membrane electrolyte in PEM fuel cells typically plays two major roles: effectively separating both fuel and oxidant, preventing mixing; and transporting protons from the anode to the cathode to complete the redox reaction chemistry. This means that the membrane electrolyte should provide strong mechanical, chemical, and electrochemical stability and low gas permeability over a wide range of operating conditions. In addition, membranes are required to have high proton conductivity at low to medium temperatures (sub-zero to 90°C). Typically, an ionic conductivity of 90–100 mS/cm is an acceptable and useful range for a number of applications in the portable, stationary, and mobile classifications, with membrane thicknesses ranging from 20 μm to 200 μm. Thicker membranes are currently preferred, due to the desire for less fuel crossover (in portable applications) and greater durability over 40,000 h (in stationary applications). Transportation applications require thinner membranes to achieve higher power density with a durability of over 5000 h. To date, PFSA membranes are the membranes of choice for PEM fuel cell systems, since their robustness, durability, and well-balanced physicochemical properties meet PEM requirements. Among the known PEM membranes (fluorinated and nonfluorinated), Nafion® is still considered the benchmark material against which most results are compared.[8–10]

Perfluorosulfonic Acid Membranes

The development of PFSA membranes has a long and rich history dating to the discovery of poly(tetrafluoroethylene)

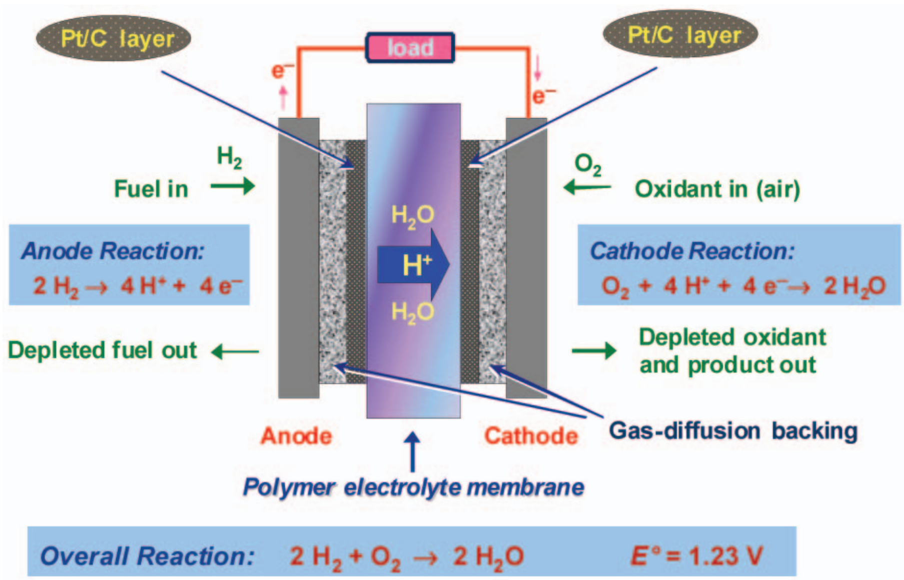


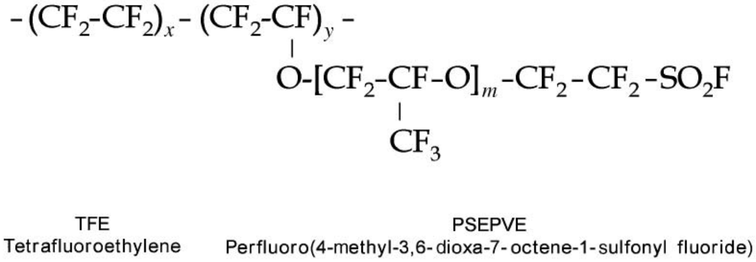
Figure 1. Schematic representation of the operating principles for polymer electrolyte membrane fuel cells.

(PTFE) in 1938. Nafion® was originally developed for chlor-alkali applications in early 1962, and later the functional group of the side chain was modified from a weaker acid to a stronger acid to suit fuel cell applications. As mentioned earlier, its first use in a fuel cell was in 1966 with its successful demonstration in NASA's space program.

Nafion® is a copolymer of TFE (tetrafluoroethylene) and vinyl ether [perfluoro (4-methyl-3,6-dioxa-7-octene-1-sulfonyl fluoride)]. Its chemical structure in nonionic form is shown in Structure **1**. Upon further chemical treatment with a base, followed by an acid, the polymer is converted from a nonconducting film ($–SO_2F$ form) to a highly conducting ($–SO_3H$ form) ionomer membrane.[4,11]

The perfluorinated backbone (TFE) imparts a chemical and thermal stability that is rare in nonfluorinated polymers. The pendant sulfonic acid ($–SO_3H$) group imparts strong acidic characteristics for facile proton transport. The acid capacity, or membrane equivalent weight (EW), of the membrane is determined by the composition of the vinyl ether and can be typically produced from 0.67–1.25 milliequivalents per gram, corresponding to 1500–800 EW. The proton conductivity of the membrane is strongly dependent on the water content in the membrane structure. The acid capacity strongly affects the water uptake and, therefore, the conductivity of the final membrane, as shown in Table I.[12] An EW range from 800–1100 is preferred for all the practical fuel cell applications considered today because it produces the maximum ionic conductivity.

The successful demonstration of PEM fuel cell operation with Nafion® membranes stimulated other fluoropolymer producers to develop stable PFSA membrane structures. Asahi Kasei Corp. (formerly Asahi Chemical), Asahi Glass Co., and Dow Chemical Co. introduced Aciplex®, Flemion®, and Dow membranes, respectively. A chemically inert PFTE backbone is common to all of these membranes; however, their side-chain structures are different, as described in Table II.[13] All of the membranes are currently available in the commercial market except the Dow membrane, which is no longer offered. A recent article[14] lists the commercially available membranes and their dispersions for fuel cell applications.



*Structure **1**. Chemical structure of Nafion® polymer. For the commercial product possessing an acid capacity, or membrane equivalent weight (EW), of 1100 EW, subscripts in the structure are* x = 6, y = 1, *and* m = 1.

Composite Perfluorosulfonic Acid Membrane Structures

Membranes based on neat PFSA ionomer have a tendency to swell undesirably when exposed to water, leading to poor handling and mechanical properties. This issue becomes more severe with thinner membrane structures, particularly at elevated temperatures. In the early 1980s, reinforcement technologies were developed to improve the mechanical stability and durability of perfluorinated membranes, particularly aiming at chlor-alkali electrolysis applications. PTFE-based woven fabrics and microfibrils were widely used for reinforcement,[15–18] due to their chemical inertness and excellent compatibility with fluorinated ionomer structures. In 1995, W.L. Gore & Associates introduced the Gore-Select® membrane, which is a microreinforced composite structure of expanded PTFE and perfluorosulfonic acid ionomer.[19] A more robust and thinner membrane, as thin as 5 μm, was produced by this technique, allowing the fuel cell to achieve high power without sacrificing longevity and durability. Recently, Asahi Glass Co. reported[20] a thin, flat PTFE fibril-reinforced PFSA membrane with good mechanical strength and performance. A continuous-film production facility has been established that uses a newly developed process.[21] A comparison of reinforcement technologies is shown in Table III.

In addition, a large number of research groups are actively engaged in modifying existing PFSA membrane structures to further improve membrane functionality and durability while retaining the base membrane properties. Both physical and chemical modifications have been explored. These include impregnation of PFSA membranes with phosphoric and sulfuric acids;[22,23] inorganic materials, namely, zirconium (hydrogen) phosphate and silica;[24,25] and the development of blend composite membranes such as ionically cross-linked acid–base membranes, PFSA/polybenzimidazole, and

perfluorinated composite membrane structures.[26–28]

Partially Fluorinated and Nonfluorinated Membranes

Research and development has been very active for the past 10–20 years in search of alternatives to perfluorinated ionomer membranes to accommodate the specific needs of PEM systems from an applications point of view. In particular, the radiation-grafted membrane approach has generated significant interest, since modification of either the surface properties or the bulk properties of the polymers could be achieved with this approach. Also, this approach is unique, offering the flexibility of introducing a variety of monomers with suitable microstructural properties that would be generally difficult to obtain by classical synthesis routes.[29] Such properties include the ability to bind water at higher temperatures and withstand higher operating temperatures; the membranes also have greater mechanical strength. Perfluorinated and partially fluorinated polymers such as PTFE, Teflon® FEP (fluorinated ethylene polypropylene), Teflon® PFA (perfluoroalkoxy), Tefzel® ETFE (ethylene tetrafluoroethylene) and PVDF [poly(vinylidene fluoride)] have been widely used as host matrices for the preparation of radiation-grafted membranes.[30] Styrene was one of the commonly used graft monomers, due to its availability and its ability to be readily modified to introduce desired functionalities specific to the application. Styrene derivatives are more often preferred, due to the oxidative instability of styrene, as described earlier.

Ballard Power Systems developed a partially fluorinated low-cost membrane for fuel cell applications in the late 1990s. Trifluorostyrene and substituted trifluorostyrene copolymer compositions (the BAM3G family of membranes from Ballard Advanced Materials) performed comparably with commercial perfluorinated membranes, and more than 100,000 h of accumulated fuel cell operation have been reported in single-cell and stack configurations.[31,32]

A tremendous amount of research is currently ongoing to develop membranes with higher operating temperatures (>100°C)—especially for automobile applications—as well as methanol-impermeable membranes for portable applications at low operating temperatures (<80°C). There are several nonfluorinated polymers, based on polyaromatic and polyheterocyclic repeat units, that show distinct chemical and microstructural properties which give a new perspective to PEM fuel cells, including higher thermal and mechanical stability, ability to work with a wide range of fuels, and lower cost. Toward higher-temperature applications, polyarylene polymers such as polysulfone, poly(ether sulfone), poly(ether ketone), poly(ether ether ketone), and poly(benzimidazole) showed good thermal and mechanical stability.[33,34] However, the durability and mechanical stability of the membranes in acid form (sulfonic or phosphonic) are still a concern and need to be improved by further optimizing the architecture of the membrane (chemical composition, microstructure, etc.).

Table I: Water Uptake and Ionic Conductivity Data for Experimental and Commercial Nafion® Membranes.[12]

Equivalent Weight (g/eq)	Water Uptake (wt %)	Effective Ionic Concentration (M)	Ionic Conductivity at 23°C (S/cm)
1500	13.3	1.245	0.0123
1350	19.4	1.338	0.0253
1200	21.0	1.492	0.0636
1100	25.0	1.591	0.0902
980	27.1	1.764	0.1193
834	53.1	1.761	0.1152
785	79.1	1.539	0.0791

Note: Data are for membranes immersed into liquid water under ambient conditions. All entries correspond to experimental products except 1100 EW, which is a commercial product.

Table II: Typical Functional Monomers of Perfluorosulfonic Acid Membranes.

Membrane Type	Comonomer Structure
Nafion®, Flemion®	$CF_2 = CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$
Aciplex®	$CF_2 = CFOCF_2CF(CF_3)OCF_2CF_2CF_2SO_2F$
Dow	$CF_2 = CFOCF_2CF_2SO_2F$

Table III: Comparison of Membrane Reinforcement Technologies.

Type of Reinforcement	Mechanical Strength	Thickness of <50 μm	Smooth Surface	Content of Reinforcing Material
PTFE* porous sheet	High	Possible	Easily available	~20–30 wt%
PTFE-yarn embedded	Very high	Difficult	Available	10 wt%
PTFE-fibril dispersed	High	Possible	Easily available	~2–5 wt%

*PTFE = poly(tetrafluoroethylene).

A Comparative Membrane Durability Study in PEM Fuel Cells

A quick screening and benchmark test to determine the lifetime (chemical durability) of a membrane is the accelerated degradation testing in Fenton's reagent (a mixture of 3% hydrogen peroxide with 4 ppm ferrous iron), as described in the literature.[7,35] The test results follow first-order kinetics closely with respect to log(ion-exchange groups lost):

$$\log(\%\ \text{degradation}) = kt, \tag{1}$$

where k is a constant and t is time. The accelerated degradation testing performed in Fenton's reagent correlates very well with actual PEM lifetime data. The relative stability of PEMs, as shown in Table IV, is perfluorinated > partially fluorinated > hydrocarbon membranes.

For practical applications such as residential power units, perfluorinated membranes with no degradation in Fenton's reagent (0.000 min^{-1}) are a more desired membrane structure due to the demanding service lifetime of ~40,000 h. Membranes with a degradation rate constant of <0.020 min^{-1} are useful for portable and transportation applications requiring 1000–5000 h operating lifetimes.

Table IV: Accelerated Degradation Rate Constant for Polymer Electrolyte Membranes.

Membrane Type	Degradation Rate Constant at 68°C (min^{-1})
Polysulfone sulfonic acid	0.218
Sulfonated poly(benzimidazole)	0.211
1% divinylbenzene cross-linked polystyrene sulfonic acid	0.125
Polyphenylene sulfonic acid	0.026
6% divinylbenzene cross-linked polystyrene sulfonic acid	0.022
Phosphonated poly(benzimidazole)	0.016
Polytrifluorostyrene sulfonic acid and cross-linked polyphosphazene	0.008
Perfluorosulfonic acid	0.000

Conclusions

The requirements for polymer electrolyte membranes are demanding and keep increasing as fuel cell technology drives toward commercial development. Higher performance, greater durability, better water management, the ability to perform at higher temperatures, and flexibility in operating with a wide range of fuels are all major criteria that need to be satisfied before the widespread commercial adoption of PEM fuel cell technology can be realized. Although the perfluorosulfonic acid membrane structure offers the balanced properties preferred today, research and development are still ongoing to deliver an improved and optimized membrane structure, in view of accommodating the unique needs of each specific application.

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